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Corrosivity Characteristic (40 CFR 261.22) Identification and Listing of Hazardous Waste Under RCRA (Resource Conservation and Recovery Act), Subtitle C, Section 3001

(U.S.) Environmental Protection Agency
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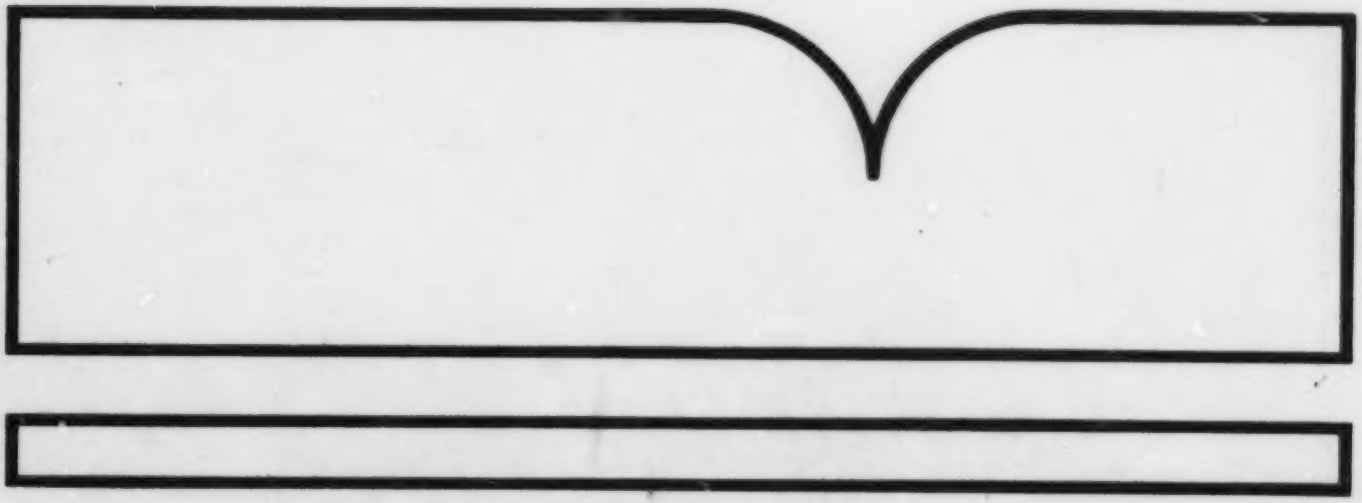

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16. Abstract (Limit: 200 words) This document is one of a series providing support for regulations issued by the U.S. Environmental Protection Agency (EPA) under Subtitle C of the Resource Conservation and Recovery Act (RCRA). The regulations represent the initial effort for nationwide control of hazardous waste from point of generation, through transportation, treatment, and storage, to point of ultimate disposal.

This document explains how EPA identified corrosiveness, the property that makes a substance capable of dissolving materials with which it comes in contact, as a hazardous waste characteristic.

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BACKGROUND DOCUMENT

IDENTIFICATION AND LISTING OF HAZARDOUS WASTE UNDER RCRA, SUBTITLE C, SECTION 3001

Corrosivity Characteristic (40 CFR 261.22)

This document (ms. 1941.24) provides background information and support for EPA's hazardous waste regulations

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May 1980

BACKGROUND DOCUMENT

RESOURCE CONSERVATION AND RECOVERY ACT

SUBTITLE C - HAZARDOUS WASTE MANAGEMENT

SECTION 3001 - IDENTIFICATION AND LISTING OF HAZARDOUS WASTE

§261.22 - Characteristic of Corrosivity

MAY 2, 1980

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF SOLID WASTE

1941.24

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I. Introduction

Subtitle C of the Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery Act of 1976 creates a comprehensive "cradle-to-grave" management control system for the disposal of hazardous waste designed to protect public health and the environment from the improper disposal of such waste. Section 3001 of that Subtitle requires EPA to identify the characteristics of and list hazardous wastes. Wastes identified or listed as hazardous will be included in the management control system created by Sections 3002-3006 and 3010. Wastes not identified or listed will be subject to the requirements for non-hazardous waste imposed by the States under Subtitle D. The Agency has determined that corrosiveness, the property that makes a substance capable of dissolving material with which it comes in contact, is a hazardous characteristic because improperly managed corrosive wastes pose a substantial present or potential danger to human health and the environment. The purpose of this document is to explain the Agency's definition of corrosive waste, to discuss the comments received on the Agency's proposed definition of corrosive waste and to discuss the changes made in response to those comments.

II. Proposed Regulation

§250.13(b) Corrosive waste.

(1) Definition - A solid waste is a hazardous waste if a representative sample of the waste:

(i) Is aqueous and has a pH less than or equal to 3 or greater than or equal to 12 as determined by the method cited below or an equivalent method.

(ii) Corrodes steel (SAE 1020) at a rate greater than 0.250 inch per year at a test temperature of 130°F as determined by the method cited below or an equivalent method.

(2) Identification method.

(i) pH shall be determined using a pH meter, following the protocol specified in the "Manual of Methods for Chemical Analysis of Water and Wastes" (EPA 625-16-74 003).

(ii) Rate of metal corrosion shall be determined using the protocol specified in NACE (National Association of Corrosion Engineers) Standard TM-01-69.

III. Rationale for the Proposed Regulation

A. Rationale for Proposing a Corrosiveness Characteristic

Corrosiveness was chosen as a characteristic of hazardous waste because improperly managed corrosive wastes present a danger to human health and the environment. Corrosion involves the destruction of both animate and inanimate surfaces. For regulatory purposes, the Agency believes that hazards associated with each must be considered. Wastes capable of destroying animate surfaces may injure human tissue while wastes capable of corroding inanimate surfaces may destroy containers holding hazardous substances, thereby enhancing the introduction of contaminants into the environment. In addition, corrosive wastes can react with other wastes to generate additional hazardous substances or dangerous amounts of heat. A number of States identify corrosiveness as a hazardous waste property in their hazardous waste regulations. These State regulations are indexed in Appendix A.

B. Rationale for Proposed Definition of Corrosiveness

1. Introduction

The Agency has chosen pH as one indicator of corrosiveness because the hydrogen ion concentration, which pH measures, is causally related to many of the hazards associated with corrosiveness (a thorough discussion of the concept of pH may be found in Reference 1). Application of a characteristic based on pH encompasses the following hazards:

- Harm to human tissue. Wastes exhibiting very high or low pH levels may cause harm to transporters

and other persons coming into contact with the waste.

o Solubilization of toxic constituents of solid waste resulting in migration to groundwater. Unregulated disposal of wastes with very high or low pH levels may contribute to the solubilization and migration of toxic constituents to groundwater, thereby threatening the health of those who use groundwater as a source of drinking water.

o Dangerous chemical reactions. Co-disposal of wastes with high or low pH levels may produce reactions resulting in dangerous heat production or generation of toxic fumes.

o Harm to aquatic life. Improper disposal of wastes exhibiting either high or low pH levels may alter the pH of surface waters to the detriment of aquatic organisms.

The Agency has chosen metal corrosion rate as another expression of corrosiveness because the metal corrosion rate indicates the ability of a corrosive waste to eat through its container and escape to the surrounding area where it may react with nearby wastes to release hazardous substances or corrode other containers holding hazardous wastes. Available information reveals that hazardous wastes are frequently stored, transported, or disposed in metal containers. Application of a characteristic based on metal corrosion rate

encompasses hazards associated with the escape of corrosive wastes from their containers to the surrounding area.

The various hazards covered by the proposed corrosiveness characteristic are discussed below in greater detail.

2. Effects of Improper Disposal of Wastes Exhibiting High or Low pH Values

(a) Injury to Humans

Wastes exhibiting very high or low pH levels may cause harm to persons who come into contact with the waste. Acids cause tissue damage by coagulating skin proteins and forming acid albuminates. Strong bases or alkalis, on the other hand, exert chemical action by dissolving skin proteins, combining with cutaneous fats and severely damaging keratin. Alkali burns tend to be progressive due to the formation of soluble alkaline proteinates and are therefore more dangerous than acid burns which may be limited by the insolubility of acid albuminates. In each type of burn, the hydrogen ion and hydroxyl ion concentration is a factor related to injury.(2) Studies indicate that pH extremes above 11.5 and below 2.5 generally are not tolerated by human corneal (eye) tissue (3).

Substances most frequently implicated in damage to human tissue in occupational settings are sulfuric, hydrochloric, hydrofluoric, nitric, acetic, carbolic, formic and oxalic acids and ammonia, caustic soda, and caustic potash (4,5). EPA files contain descriptions of several incidents in which contact with corrosive wastes resulted in tissue damage (6). Three incidents are described in Appendix B.

(b) Solubilization of Toxic Contaminants

Low or high pH levels significantly promote the solubilization of certain toxic substances such as heavy metals. Once solubilized, these hazardous substances can migrate to a groundwater body where, under proper conditions, they can move great distances without significant attenuation of toxicity. Since approximately half the population of the United States depends on groundwater as a source of drinking water, this enhanced migration of toxic constituents warrants serious concern (7). A study of 50 land disposal sites in which industrial wastes had been placed revealed that sub-surface migration of hazardous substances is prevalent. Migration of toxic heavy metals was confirmed at 30 of the sites; at 26 of the sites levels in excess of EPA drinking water standards were discovered (8). Damage resulting from contamination of groundwater by toxic inorganic substances is well documented. Reference 6 contains many examples of injury to human health and the environment attributable to contaminated groundwater.

The tendency of toxic waste constituents to solubilize in response to increased or decreased pH levels is illustrated by the theoretical solubilities of heavy metal compounds in aqueous solutions at various pH values. For instance, calculations demonstrate that a drop in pH from 4.0 to 2.0 should increase the solubility of red mercury oxide (HgO) or of chromium hydroxide ($Cr(OH)_3$) in water approximately one hundred times (9). In general, compounds of mercury tend to solubilize in an acidic environment while chromium, cadmium,

lead and silver compounds may be soluble in either acidic or alkaline media. Compounds of arsenic and selenium solubilize more readily in an alkaline environment. (9,10,11)

Because the solubilization of waste stream components is a complex phenomenon dependent upon factors such as the ionic strength of the medium, the oxidation potential, and the presence of complexing and chelating agents and available anions, the above theoretical solubilities--which are applicable to pure compounds in simple systems--cannot readily be extrapolated to complex waste systems. However, these figures clearly reveal trends in the relationship between pH and solubility. Thus, although limits which precisely define the low or high pH values at which solubilization of the various heavy metal compounds occurs in all wastes cannot be established in reliance on these figures, in general, there is greater potential for solubilization as pH values approach the lower and upper ends of the scale.

(c) Dangerous chemical reactions

Co-disposal of incompatible wastes may lead to the following harmful reactions: 1. heat generation, 2. fire, 3. explosion, 4. formation of flammable gases, 5. volatilization of toxic or flammable substances, 6. formation of substances of greater toxicity, 7. formation of compounds sensitive to shock and friction, 8. pressurization in closed vessels, 9. formation of toxic fumes, 10. dispersal of toxic dusts, mists and particles, and 11. violent polymerization (12). Improper disposal of wastes exhibiting high or

Intentionally Blank

low pH levels is often associated with these adverse consequences. Toxic and flammable gases, for instance, may be generated when cyanides or sulfides are mixed with acids (13). Violent chemical reactions can occur when strong acids are mixed with strong bases. Appendix C contains case histories documenting damage to human health, the environment and property caused by mixing acidic or caustic wastes with other wastes. Appendix D lists possible adverse consequences resulting from reactions between acids or bases and other classes of compounds.

It is difficult to establish an exact pH value at which wastes of varying composition pose a hazard, but certainly the tendency to cause harmful chemical reactions becomes more pronounced at the extremes of the pH scale. By any estimation, highly acidic or highly alkaline liquid wastes have the potential to cause chemical reactions which can have an adverse effect on human health and the environment.

(d) Injury to aquatic life

Improper disposal of wastes exhibiting high or low pH may alter the pH levels of surface waters, resulting in harm to aquatic life. Studies indicate that the optimum pH range for freshwater fish is 6.5 - 9.0; an increase or decrease of 2 pH units beyond the optimum causes severe effects. Bioassays conducted on the fathead minnow revealed that a generation maintained in environments with pH values of 4.5 and 5.2 were deformed and exhibited abnormal behavior. As Table 1 shows, pH levels of 11.0 or 3.5 are fatal to all species of

fish. At pH levels below 3 and above 12, very few organisms are capable of survival (14).

Addition of wastes exhibiting low or high pH levels to surface waters can also increase the toxicity of substances in the water. Acidification of the water can result in the release of free carbon dioxide in toxic quantities, and a drop of about 1.5 pH units can cause a thousand-fold increase in the acute toxicity of a metallocyanide complex (14). In addition, alteration of the surface water pH is capable of affecting the productivity of food organisms which fish and wildlife need to survive. Appendix E lists incidents of damage to aquatic life caused by wastes exhibiting high or low pH values (6).

(e) EPA's final pH limits

As noted above, the Agency has chosen pH as one measure of corrosiveness because pH provides an easily-measurable, multi-purpose indicator of several potentially hazardous conditions. In its proposed regulation, the Agency defined aqueous wastes with pH levels below 3.0 and above 12.0 as being hazardous. These limits were chosen in an attempt to balance the following considerations: sensitive human tissue may be damaged when contacted with substances exhibiting pH levels below 2.5 or above 11.5; strongly acidic or basic conditions significantly enhance the solubilization of toxic contaminants and are an integral cause of dangerous chemical reactions; aquatic life is adversely affected where the pH of the water is below 6.5 or above 9.0 and is virtually

non-existent in media with pH values below 3.0 and above 12.0.

In response to the proposed pH limits, a great many comments were received advocating the extension of the accpetable pH range. A number of commenters argued that the proposed upper pH limit of 12.0 would include waste lime and many lime treated wastes and sludges which generally have a pH between 12.0 and 12.5 and which can be put to agricultural and other beneficial uses. Many of these commenters suggested raising the upper pH limit to 12.5 while others suggested raising the limit to 13.0. A number of commenters argued that the proposed lower pH limit of 3.0 would include many common and innocuous substances such as cola drinks which exhibit pH levels of between 2.0 and 3.0 and many industrial wastewaters prior to neutralization which also exhibit low pH levels. Many of these commenters suggested lowering the pH limit to 2.0; others suggested lowering the limit to 1.5.

Upon consideration of these comments and after further deliberation, the Agency has decided to extend the range of acceptable pH levels by decreasing the lower limit from pH 3.0 to 2.0 and increasing the upper limit from pH 12.0 to 12.5. With respect to the upper limit, the Agency agrees with the commenters that otherwise non-hazardous lime stabilized sludges and wastes should not be designated as hazardous. Accordingly, the Agency has adjusted the upper limit to pH 12.5 to exclude such wastes from the system. Raising the

TABLE —1.—A Summary of Some Effects of pH on Freshwater Fish and Other Aquatic Organisms 8

pH	Known effects
11.5–12.0....	Some caddis flies (Trichoptera) survive but emergence reduced.
11.0–11.5....	Rapidly lethal to all species of fish.
10.5–11.0....	Rapidly lethal to salmonids. The upper limit is lethal to carp (Cyprinus carpio), goldfish (Carassius auratus), and pike. Lethal to some stoneflies (Plecoptera) and dragonflies (Odonata). Caddis fly emergence reduced.
10.0–10.5....	Withstood by salmonids for short periods but eventually lethal. Exceeds tolerance of bluegills (Lepomis macrochirus) and probably goldfish. Some typical stoneflies and mayflies (Ephemera) survive with reduced emergence.
9.5–10.0....	Lethal to salmonids over a prolonged period of time and no viable fishery for coldwater species. Reduces populations of warmwater fish and may be harmful to development stages. Causes reduced emergence of some stoneflies.
9.0–9.5.....	Likely to be harmful to salmonids and perch (Perca) if present for a considerable length of time and no viable fishery for coldwater species. Reduced populations of warmwater fish. Carp avoid these levels.
8.5–9.0.....	Approaches tolerance limit of some salmonids, whitefish (Coregonus), catfish (Ictaluridae), and perch. Avoided by goldfish. No apparent effects on invertebrates.
8.0–8.5.....	Mobility of carp sperm reduced. Partial mortality of burbot (Lota lota) eggs.
7.0–8.0....	Full fish production. No known harmful effects on adult or immature fish, but 7.0 is near low limit for Gammarus reproduction and perhaps for some other crustaceans.
6.5–7.0.....	Not lethal to fish unless heavy metals or cyanides that are more toxic at low pH are present. Generally full fish production, but for fathead minnow (Pimephales promelas), frequency of spawning and number of eggs are somewhat reduced. Invertebrates except crustaceans relatively normal, including common occurrence of molluscs. Microorganisms, algae, and higher plants essentially normal.
6.0–6.5.....	Unlikely to be toxic to fish unless free carbon dioxide is present in excess of 100 ppm. Good aquatic populations with varied species can exist with some exceptions. Reproduction of Gammarus and Daphnia prevented, perhaps other crustaceans. Aquatic plants and microorganisms relatively normal except fungi frequent.
5.5–6.0.....	Eastern brook trout (Salvelinus fontinalis) survive at over pH 5.5. Rainbow trout (Salmo gairdneri) do not occur. In natural situations, small populations of relatively few species of fish can be found. Growth rate of carp reduced. Spawning of fathead minnow significantly reduced. Molluscs rare.
5.0–5.5.....	Very restricted fish populations but not lethal to any fish species unless CO_2 is high (over 25 ppm), or water contains iron salts. May be lethal to eggs and larvae of sensitive fish species. Prevents spawning of fathead minnow. Benthic invertebrates moderately diverse, with certain black flies (Simuliidae), mayflies (Ephemerella), stoneflies, and midges (Chironomidae) present in numbers. Lethal to other invertebrates such as the mayfly. Bacterial species diversity decreased; yeasts and sulfur and iron bacteria (Thiobacillus-Ferrobacillus) common. Algae reasonably diverse and higher plants will grow.
4.5–5.0.....	No viable fishery can be maintained. Likely to be lethal to eggs and fry of salmonids. A salmonid population could not reproduce. Harmful, but not necessarily lethal to carp. Adult brown trout (Salmo trutta) can survive in pool waters. Benthic fauna restricted, mayflies reduced. Lethal to several typical stoneflies. Inhibits emergence of certain caddis fly, stonefly, and midge larvae. Diatoms are dominant algae.
4.0–4.5.....	Fish populations limited; only a few species survive. Perch, some coarse fish, and pike can acclimate to this pH, but only pike reproduce. Lethal to fathead minnow. Some caddis flies and dragonflies found in such habitats; certain midges dominant. Flora restricted.
3.5–4.0.....	Lethal to salmonids and bluegills. Limit of tolerance of pumpkinseed (Lepomis gibbosus), perch, pike, and some coarse fish. All flora and fauna severely restricted in number of species. Cattail (Typha) is only common higher plant.
3.0–3.5.....	Unlikely that any fish can survive for more than a few hours. A few kinds of invertebrates such as certain midges and alderflies, and a few species of algae may be found at this pH range and lower

upper limit to pH 12.5 should not compromise protection of human health. Although eye tissue is damaged when the pH is above 11.5, normal skin tissue is clearly less sensitive than eye tissue. Consequently, increasing the upper pH limit to 12.5 should not significantly increase the likelihood of damage to skin. Also, taking into account the many factors that might influence heavy metal solubility and causation of harmful chemical reactions, an increase of 0.5 pH unit is not expected to significantly compromise protection against these two hazards.

With respect to the lower limit, the Agency is not necessarily in agreement with the comments that such "innocuous" substances as cola drinks, if disposed of in a landfill, will have only benign consequences. Nevertheless, it agrees with the comments that 2.0 is a better justified lower pH limit than 3.0. The Agency originally chose 3.0 as its lower limit based on tissue damage and heavy metal solubilization. Although studies on corneal tissue demonstrated that injury was sustained on contact with substances exhibiting pH levels below 2.5, the proposed pH limit was set at 3.0 to provide an extra margin of protection against heavy metal solubilization. Corneal tissue, however, is more sensitive than skin tissue so reducing the lower pH limit to 2.0 should still allow adequate protection against skin injury. Similiarly, lowering the pH limit to the avowedly highly acidic level of 2.0 ensures that the limit is more likely to encompass those wastes which tend to solubilize toxic substances and cause harmful reactions.

3. Effects of Improper Disposal of Wastes Capable of Corroding Metal.

Wastes which have the capacity to corrode metals can corrode their containers during transportation, storage or disposal and escape into the surrounding area. If such corrosive wastes are toxic, their escape can cause direct injury to persons handling the waste and can contaminate the environment. If such wastes exhibit low or high pH, their escape can result in all the hazards associated with low or high pH, as discussed above. Wastes capable of corroding metals can also cause the corrosion of other containers in which hazardous wastes are stored, resulting in the leakage of those wastes into the environment. This unplanned leakage can result in injury to persons handling the wastes and the contamination of the environment.

Metal corrosion is a complex process; a more detailed discussion of its mechanisms may be found in Reference 15. Factors which influence the rate of corrosion include temperature, the metal(s) involved and aeration, composition and pH of the corrosive medium. For example, a corrosive material with a pH less than 4.0 will cause iron to dissolve rapidly accompanied by evolution of hydrogen. At pH 4.0-9.5 the rate of attack is usually low and fairly constant then decreases to a minimum at pH 12.0. Increases in pH above 12.0 accelerate dissolution of the metal but the corrosion rate is generally much less than that occurring under acidic conditions. In practice, alkaline solutions do not severely damage steel.

The presence of dissolved salts may also accelerate or inhibit corrosion; chloride and sulfate ions interfere with development of protective films and contribute to the breakdown of passive films already in existence while calcium and bicarbonate ions tend to limit attack. The amount of dissolved oxygen is another important element because oxygen stimulates the corrosion process. Temperature affects corrosion by influencing the chemical composition and physical properties of the corrosive solution, the nature of deposits and the behavior of the metal.

The Department of Transportation has defined a corrosive material as one that corrodes a low carbon steel (SAE 1020) at a severe rate, i.e., greater than 0.250 inch per year at a test temperature of 130° F (49 CFR 173.240). The rate of 0.250 inch per year was selected by DOT because experience indicated that it represents a severe rate of corrosion. SAE 1020 steel was chosen as a test material by DOT because it is used frequently in the manufacture of steel drums utilized in transportation, and the 130° test temperature was selected because that level may be encountered during transportation of hazardous materials.

EPA files contain numerous descriptions of damage incidents involving the use of steel drums to store, transport and dispose of hazardous waste. The Agency believes that the rate at which a waste corrodes a material commonly used in container construction is a suitable measure of the hazardousness of the waste. The DOT metal corrosion standard was

adopted because it represents an appropriately severe rate of corrosion, and the required test conditions adequately reflect conditions likely to be encountered during transportation, storage and disposal of wastes. An additional consideration is the desire of the Agency to maintain consistency with other regulations whenever practicable.

4. Additional Considerations for Development of a Corrosiveness Characteristic.

(a) Direct Measurement of Tissue Damage

The Agency considered proposing a corrosive characteristic which would directly address tissue damage. A standard technique referenced by Federal agencies and several States employs the application of the suspected corrosive to the bare, intact skin of albino rabbits. The animals are exposed for a specified period of time after which an assessment of tissue damage is made (16, 17, 18). Conduction of the test requires maintenance of special facilities and the use of skilled personnel to evaluate the extent of injury. The Agency believes that performing this type of testing on each waste stream would add little to the scope of the corrosivity definition and be unnecessarily burdensome to many members of the regulated community. For waste disposal purposes, relating tissue damage to an easily measurable characteristic such as pH is the more practical approach because the hydrogen ion or hydroxyl ion concentration is related to the degree of injury. The pH provision will not encompass all substances that damage tissue, but corrosive substances often display

other hazardous characteristics that will bring them into the hazardous waste net. For instance, corrosive metal salts such as the arsenicals, chromates and mercurials probably will be covered by the toxicity characteristic.

(b) Acidity and Alkalinity

During the development of these regulations, it was suggested that the corrosiveness characteristic should address the percent acidity or alkalinity of the wastes in addition to the pH. Percent acidity or alkalinity provides an indication of the capacity of a liquid waste to resist a change in pH (buffering capacity). Because the Agency did not have adequate information concerning the necessity of addressing acidity and alkalinity as a component of its hazardous waste definition and had no technical basis upon which to establish levels of hazard, comments on this issue were solicited in the preamble to the proposed regulations. A few comments favored adding a acidity/alkalinity provision to the pH characteristic because it would provide useful information for disposal purposes. Most comments, however, stated that addressing acidity and alkalinity would not add significantly to the determination of hazard and would necessitate the use of somewhat more costly and complicated measurement techniques than pH alone.

The Agency agrees that the addition of an acidity/alkalinity determination to the pH provision of the corrosivity definition is not necessary. Although acidity and alkalinity have some

bearing on the manner in which these wastes are disposed, they add little to the assessment of the hazard posed during transportation, storage and initial disposal. Additionally, because the ability of a waste to retain low or high pH is as much a function of its disposal environment as of its percent acidity/alkalinity the Agency knows of no scientifically valid basis upon which to establish hazardous threshold levels of percent acidity/alkalinity. Therefore the Agency has elected not to include percent acidity/alkalinity in the definition.

(c) Corrosiveness of Solids

The Agency considered making the pH provision of the corrosiveness characteristic applicable to wastes in solid form which are capable of forming aqueous solutions of low or high pH once disposed. Estimates in the Agency's possession, however, indicate that approximately 90% of all hazardous wastes are in liquid or in semi-liquid form (19). The Agency therefore solicited comments in the preamble to the proposed regulations on the desirability of including solids in the pH provision of the corrosiveness characteristic. The few comments that were received in response to this inquiry favored the inclusion of solids in the corrosiveness definition, but did not describe situations where damage would be likely to occur as a result of improper disposal of such wastes.

Upon consideration of these comments, the Agency has concluded that there is no demonstrated need to address

solids which may become corrosive in its corrosiveness definition at this time. Liquid wastes constitute by far the greater percentage of hazardous wastes and have a more immediate potential to effect mobilization of toxic substances in the environment. Furthermore, corrosive solids are not as likely to cause problems as liquid wastes because the ability of a solid to form an aqueous solution of high or low pH varies with its physical and chemical characteristics and the management conditions. The RCRA prohibition against open dumping coupled with the requirements for proper management of both hazardous and non-hazardous wastes under the Section 3004 and 4004 regulations will reduce the risk of damage to the environment from these wastes. Additionally, some corrosive solids will probably be subject to the regulations because they exhibit other hazardous characteristics, e.g., toxicity. EPA will continue to seek additional information on the hazards posed by wastes in solid form capable of generating solutions with high or low pH and will consider specific regulatory measures if the need for more control becomes apparent.

IV. Test Methods

A. pH

pH is measured by colorimetric or electrometric means. Colorimetric techniques have severe limitations which make them inappropriate for the pH determination of wastes. They are subject to severe interference from turbidity, color, high saline content, colloidal matter, free chlorine and

various oxidants and reductants. In addition, a single indicator is often limited to a relatively narrow pH range.

An acceptable method of pH measurement by electrometric technique is described in Methods for Analysis of Water and Wastes (EPA-600/4-79-020). pH is determined using either a glass electrode with a reference potential or a combintion electrode. The glass electrode is relatively free from most types of interference, but may display impaired response under certain conditions. The alkaline error encountered at pH values above 10 can be diminished by using "low sodium error" electrodes. Ambient temperature and the temperature of the sample also influence electrometric measurement. The effect caused by the alteration in electrode output at various temperatures can be controlled by using instruments with a temperature compensation feature. The variation in temperature of the individual samples cannot be controlled; therefore, sample temperature and pH should be recorded as each sample is measured. Other sources of interference include coatings of oily material or particulate matter on the electrode and reduction of electrode life due to attack by solutions which corrode glass. These can be minimized by proper cleaning of the electrode.

The form of the substance to be measured should be taken into account during a determination of pH. Blockage of the liquid junction between the salt bridge and the test solution must be prevented when measuring the pH of suspensions, sols

or gels. Suspensions of highly charged sediments such as soils or ion exchange resins may not give a true pH reading; the solution should be allowed to settle and the pH of the supernatant measured (20).

Measurement of pH is a routine laboratory technique for which a wide variety of instruments is available. A precision of $\pm$ 0.02 pH unit and an accuracy of $\pm$ 0.05 pH unit can be achieved, but $\pm$ 0.1 pH unit represents the limit of accuracy under normal conditions. Therefore, pH values should be reported to the nearest 0.1 pH unit (21).

B. Metal Corrosion

For purposes of hazardous waste definition, EPA believes that it should employ a metal corrosion test which indicates the general corrosion of a metal frequently used in the manufacture of hazardous waste containers. Coupon corrosion testing is designed for this purpose. Other procedures are available to test for special metallurgical phenomena, but they are more useful in the development of specific container standards.

NACE Standard TM-01-69 describes a simple immersion test to determine rate of corrosion. The procedure is not completely standardized because it was designed to test the suitability of metals for a variety of uses. Although the standard is commonly employed as a method to detect the corrosiveness of a solution of known composition on a certain metal, its flexibility makes it suitable for determining the corrosiveness of a mixture of unknown composition such as a waste.

The NACE standard gives recommended practices for sample preparation, type of equipment, and test conditions. Duplicate metal coupons are first cleaned and weighed. The solution is placed in an apparatus consisting of a flask, a reflux condenser, a thermowell, a heating device and an appropriate specimen support system. The preferred minimum volume to area ratio is 40 millimeters of solution per square centimeter of specimen. The specimens are exposed to the test solution at a temperature of 55°C (130° F). Corrosion should not be allowed to proceed to a point where the original specimen size or exposed area is drastically reduced or the metal is perforated. Aeration is unnecessary, and corrosive constituents do not need to be replenished because metal waste containers are likely to be in contact with a limited amount of solution.

At the end of the exposure period, the coupons are removed from the test environment, then cleaned and weighed. The corrosion rate can be calculated by the following equation:

$$\text{millimeters per year (mmpy)} = \frac{\text{weight loss} \times (0.268)}{(\text{area})\ (\text{time})}$$

Weight loss is in milligrams, area is square inches of exposed metal surface and time is hours exposed

V. Comments on the Proposed Regulations

Generally, comments on the proposed regulation can be placed in several broad categories. The greatest number of responses concerned the proposed pH limits. Others addressed

the establishment of a characteristic that would encompass acidity and alkalinity, solids which form aqueous solutions of high or low pH or a direct measure of tissue damage. A few comments suggested that neither pH or the metal corrosion provision is appropriate for defining corrosion.

A. pH Limits

- The proposed pH limits are unnecessarily restrictive.

A great many comments advocated extending the acceptable pH range. These comments have been fully addressed above and need not be further addressed here.

- The Agency should define the term "aqueous" waste.

The pH characteristic is applicable only to aqueous waste because pH relates to the hydrogen ion activity in a solution. A few comments suggested that EPA specifically define "aqueous" in terms of viscosity or percent water. The Agency has not developed a specific definition because of the widely varying physical and chemical properties which influence the form of wastes. Those who generate, treat, store or dispose of a waste can best determine whether it is in a suitable form for pH measurement.

- Corrosiveness is not typically defined in terms of pH.

A few comments stated that, in the correct technical sense, corrosion is an electrochemical reaction between the environment and a metal surface; pH is not, therefore, a standard measure of corrosiveness. The Agency does not agree that the concept of corrosiveness is so limited. As stated

previously, the Agency believes that the definition of a corrosive waste should embrace both hazards associated with metal corrosion and hazards associated with high and low pH. A waste exhibiting either a very high or very low pH may corrode the skin tissue of waste handlers. pH is also a significant factor in solubilization of heavy metal salts which results in increased mobility of toxic substances in the environment. In addition improper disposal of wastes exhibiting very high or low pH values can cause dangerous chemical reactions in landfills. Establishing pH limits appears to be the most effective way to address the various concerns.

- o pH limits should address organic wastes.

Some comments suggested that the pH limit should address organic wastes. If an organic waste is in an aqueous solution it will be subject to the pH provision.

B. Tissue Damage

- o The regulations should address tissue damage in a more direct manner.

Some comments stated that the corrosiveness of some substances which damage human tissue will not be adequately indicated by a pH measurement. As discussed previously, the Agency considered adopting the skin corrosion test referenced by the Food and Drug Administration and the Department of Transportation, but concluded that relating tissue damage to an easily measurable characteristic such as pH is a more reasonable approach for waste disposal purposes. Not all

substances capable of damaging human tissue will be encompassed by the pH provision. However, wastes may display one or more of the other hazardous characteristics or possess qualities which cause them to be listed as hazardous wastes. Several comments mentioned the Consumer Product Safety Commission detergent toxicity survey which found a relationship between pH and corrosiveness to tissue, but did not find a correlation strong enough to use for regulation of detergent products. The Agency believes that inasmuch as its pH provision addresses not just tissue damage but also such things as the solubilization of toxic materials and the causation of dangerous chemical reactions, use of pH as a barometer of tissue damage is both reasonable and justified.

C. Acidity/Alkalinity

- The regulations should address acidity and alkalinity.

Several comments addressed the addition of acidity and alkalinity to the pH criterion. These comments have been fully addressed above and need not be further addressed here.

D. Corrosiveness of Solids

- The regulations should address solids which may form aqueous solutions of high or low pH and solids which are corrosive to metal and human tissue.

A number of comments addressed the desirability of making the pH provision of the corrosiveness characteristic applicable to solid wastes as well as liquid wastes. These comments have been fully addressed above and need not be further addressed

here.

E. Metal Corrosion Provision

The Agency received a number of comments on the metal corrosion provision, many of which wanted to inject management practices into the metal corrosion standard. Some commenters felt that the metal corrosion test should apply only to containerized waste. Others believed that the test should be performed on containerized materials using the specific material from which the container is made as the test material.

The Agency has made the metal corrosion provision applicable to non-containerized wastes because such wastes are capable of corroding the containers of co-disposed wastes. The Agency has chosen steel as a test material because steel is commonly employed in the manufacture of steel drums and steel drums are frequently used to store and dispose of hazardous waste. Using the specific material from which a generator's containers are made as the test material for the metal corrosion test would make the hazardousness of the waste too dependent upon the actual management practices employed by the generator. It must be emphasized that the metal corrosion provision constitutes an attempt to define which wastes are hazardous if improperly managed, that is, which wastes are hazardous under some likely mismanagement scenario. The definition is not an attempt to set out standards for proper management; this is accomplished by the Section 3004 regulations.

One commenter remarked that the 130° test temperature specified by the metal corrosion provision is too high. The Agency picked that temperature to reflect conditions encountered during transportation of hazardous wastes and in landfills. Studies show that temperatures in that range are encountered in landfills. (22, 23).

Several comments were made concerning the choice of steel as a test material. One comment stated that the corrosion rate of steel is influenced by many factors. The Agency is aware that corrosion is a complex phenomenon and has chosen the NACE test because that test, by giving a general indication of the ability of a waste to corrode metal, ably accomodates the many factors influencing corrosion. One comment states that otherwise harmless wastes such as salt water will corrode steel but provides no information on the corrosion rate of such harmless wastes. Lacking such information, the Agency is unable to evaluate the merit of this contention. In any event, the Agency is convinced that any waste which exhibits as severe a corrosion rate as 6.35 mm/year must be segregated from containers holding other hazardous wastes during transportation, storage and disposal.

One comment suggested that the metal corrosion test is unnecessary because steel drums will invariably corrode in a landfill environment. The Agency disagrees. The metal corrosion provision is designed to address hazards associated with transportation, storage or disposal as well as hazards

associated with placing containerized wastes in landfills. Furthermore, the Agency doubts that the corrosive influences found in a landfill exert anything close to the corrosive effect exerted by wastes exhibiting a corrosion rate of 0.250 inch per year.

- When an aqueous waste is extremely thick or is not amenable to stirring to obtain homogeneity, the solids should be allowed to settle and the pH of the supernatant measured.

Some comments suggested that when an aqueous waste is extremely thick or is not amenable to stirring to obtain homogeneity (as in the case of a slurry), the solids should be allowed to settle and the pH test applied to the supernatant liquid. The Agency finds this an acceptable practice to prevent interference caused by blocking of the electrode.

G. General Comments

- Permit writers should judge the hazard associated with wastes exhibiting high or low pH levels on a case-by-case basis.

One comment suggested that permit writers should judge the hazard associated with pH on a case-by-case basis. The purpose of RCRA Section 3001 is to define a hazardous waste in terms of physical, chemical and biological properties. Actual management standards will be established under Section 3004. Regulations promulgated pursuant to Section 3005 will provide sufficient flexibility in the permitting process to accommodate various management methods for hazardous wastes as long as those methods protect human health and the environment.

- Corrosive wastes should not be classified as hazardous if properly managed.

Several comments argued, in effect, that corrosive wastes which are properly managed or which do not otherwise fit the mismanagement scenario envisioned by the corrosiveness definition should not be classified as hazardous. One comment stated that corrosive wastes should be classified as hazardous depending on the containers used. Other comments argued that the definition should be revised to exclude wastes which are not transported, stored or disposed with other wastes. As noted above, in defining hazardous corrosive waste, the Agency has attempted to reach those wastes which are hazardous if mismanaged under some likely mismanagement scenario. The purpose of the definition is to bring such wastes into the hazardous waste management system set up by Sections 3002, 3003, 3004, and 3005 of the Act -- not to specify management practices. If management practices were made part of the definition so that properly managed wastes were excluded from the definition, the effectiveness of the management system created under Sections 3002, 3003, 3004, and 3005 might well be vitiated, since properly managed wastes would be excluded at the outset from the continuing supervision and control provided by the management system thus prejudicing the Agency's ability to ensure continued compliance with these proper management practices. The regulations under Section 3004 and 3005 will be sufficiently flexible to

accomodate wastes which are properly managed or which otherwise don't fit the mismanagement scenario envisioned by the corrosiveness definition.

In a closely related comment, one commenter stated that since disposal of liquids in landfills is not permitted, liquid corrosives do not really present a hazard. This argument is largely circular because if liquid corrosives were not classed as hazardous, they could readily be disposed of in landfill environments.

- o Specify measurement of pH within $\pm$ 0.5 pH units.

One comment suggested that the Agency should specify measurement of pH within $\pm$ 0.5 pH units. Under normal conditions, pH should be measured to the nearest 0.1 of a unit. Measurement can be made more precisely if necessary. The Agency sees no reason to permit measurement within $\pm$ 0.5 pH units.

Metal Corrosion

- o NACE Standard TM-01-69 is not completely standardized and permits variation in a number of test conditions.

One comment argued that the NACE Standard TM-01-69 permits variation in a number of test conditions and that therefore the test is not clearly enough defined. The Agency recognizes that this is the case and, to correct the problem, has more clearly defined the appropriate test conditions. A description of these conditions is found in "Test Methods for Evaluating Solid Waste" SW-846.

- The generator should be allowed to use a corrosion rate given in the Corrosion Data Survey as a substitute for employing the NACE test.

One comment argued that the generator should be allowed to use a corrosion rate given in the Corrosion Data Survey as a substitute for the NACE test. The Agency does not agree. The Corrosion Data Survey gives corrosion rates for water dilutions of pure compounds (24). Contaminants, however, may exert a significant effect on corrosion rate. Because wastes are often complex mixtures rather than simple aqueous solutions, the Agency believes that actually performing the NACE test provides a more appropriate indication of hazard.

- The corrosiveness of the waste is to be determined at the point of generation. The corrosiveness characteristic should not apply to wastes which lose their corrosive nature after a certain period of time.

One comment asked whether the corrosiveness of the waste is to be determined at the immediate point at which it becomes a waste or in the form in which the generator disposes of it. Another comment suggested that the corrosiveness characteristic should not apply to wastes which lose their corrosive nature after a certain period of time. A waste is defined as hazardous at the point of generation unless it is piped directly to a treatment facility. Where wastes are stored before treatment or transported in other than a closed pipe system, the Agency believes that the hazardous waste characteristics must apply in order to protect human health and the environment. The Agency has not exempted from the

corrosiveness characteristic wastes which lose their corrosive nature after a period of time because (a) such wastes present a hazard, at least initially (b) the Agency has no criteria for determining which corrosives will persist and which will not.

- The corrosiveness characteristic should not be applicable to certain wastes.

Several comments stated that the corrosiveness characteristic should not be applicable to certain wastes. Some comments stated that the corrosivenness characteristic should not apply to fly ash since it is not containerized and its disposal does not involve human contact. As discussed previously, for the purpose of hazard definition the corrosiveness characteristic applies whether a waste is containerized or not or whether waste handlers are involved. If fly ash does not corrode steel, and exhibits a pH less than 12.5 then it is not a hazard within the meaning of the corrosiveness characteristic.

It was suggested that organic acids be exempted from application of the corrosiveness characteristic because they tend to degrade under landfill conditions. Even if degradation does occur the Agency is concerned with storage and transportation as well as disposal. Furthermore, Appendix D illustrates that unregulated co-disposal of organic acids and other substances can result in harmful consequences such as generation of heat or toxic gases, fire and explosion.

Some comments suggested exempting drilling fluid because

the pH of the material decreases when it is placed in a reserve pit. No data were given on the pH of drilling fluid before discharge to the pit. The comment contends that this is a treatment procedure. As such, it may be acceptable under Section 3004 standards. Hazardous waste definition standards under Section 3001, however, are applicable at the point at which a waste is generated. The Agency sees no reason why the corrosiveness characteristic should not be applicable to drilling fluids if they meet the provisions of the characteristic.

- Separate the pH and metal corrosion provision in the regulations because they measure different effects.

One comment suggested separating the pH and metal corrosion provisions in the regulations because they measure different effects. The Agency sees no reason for doing this. Each provision covers a type of corrosion, i.e. corrosion to living tissue or corrosion to metal surfaces and both types are properly subsumed under one characteristic.

- Determine the overlap between the pH provision and the metal corrosion provision to see whether the metal corrosion provision can be eliminated.

One comment suggested that the Agency determine the overlap between the pH provision and the metal corrosion provision to determine whether the metal corrosion provision can be eliminated. The Agency sees no justification for this approach. While pH is an important factor in metal corrosion, the two provisions address different effects and are not necessarily mutually inclusive.

H. Summary of Data on the Metal Corrosion Test Published in the NUS Report* and Response to Comments Received on that Noticed Report

As part of the testing program carried out under this contract, EPA had a sample of spent pickle liquor and a sample of spent caustic tested by two laboratories to determine the rate at which these wastes corrode SAE 1020 steel. As expected, the coupons exposed to the spent caustic showed no appreciable corrosion. (Alkaline wastes are not especially corrosive to steel.) The coupons exposed to the spent pickle liquor corroded at rates of 509 inches per year in Lab J and 220 inches per year in Lab K. The difference in corrosion rates is attributed to variations in test conditions and the extreme corrosiveness of the test medium. The corrosiveness characteristic provides that a liquid waste is hazardous if it has a corrosion rate greater than 0.25 inch per year.

One commenter stated that the difference between the corrosion rate of the spent pickle liquor samples indicated that the NACE test is not reproducible. The Agency does not agree. The reproducibiity of this test cannot be determined on the basis of the NUS test performance since variability is to be expected at the extremely high corrosion rates found by the two laboratories. The important point is that the spent pickle liquor in both samples flunked the corrosivity

*"Evalution of Solid Waste Extraction Procedures and Various Hazard Identification Tests (Final Report)", NUS Corporation, September, 1979.

characteristic by three orders of magnitude and thus would be considered a hazardous waste.

VI. Promulgated Regulation

The Agency has reviewed the comments on the proposed regulations and agrees that the pH limits should be lowered from 3.0 to 2.0 and increased from 12.0 to 12.5. The corrosiveness characteristic is now defined as follows:

§261.22 Characteristic of corrosivity

(a) A solid waste exhibits the characteristic of corrosivity if a representative sample of the waste has either of the following properties:

(1) It is aqueous and has a pH less than or equal to 2 or greater than or equal to 12.5, as determined by a pH meter using either the test method specified in the "Test Methods for the Evaluation of Solid Waste, Physical/ Chemical Methods"* (also described in "Methods for Analysis of Water and Wastes" EPA 600/4-79-020, March 1979), or an equivalent test method approved by the Administrator under the procedures set forth in §§260.20 and 260.21.

(2) It is a liquid and corrodes steel (SAE 1020) at a rate greater than 6.35 mm (0.250 inch) per year at a test temperature of 55°C (130°F) as determined by the test method specified in NACE (National Association of Corrosion Engineers) Standard TM-01-69** as standarized in "Test Methods

*This document is available from Solid Waste Information, U.S. Environmental Protection Agency, 26 W. St. Clair Street, Cincinnati, Ohio 45268.

**The NACE Standard is available from the National Association of Corrosion Engineers, P.O. Box 986, Katy Texas 7740

for the Evaluation of Solid Waste, Physical/Chemical Methods," or an equivalent test method approved by the Administrator under the procedures set forth in §§260.20 and 260.21.

(b) A solid waste that exhibits the characteristic of corrosivity, but is not listed as a hazardous waste in Subpart D, has the EPA Hazardous Waste Number of D002.

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CORROSIVENESS - STATE IDENTIFICATION CRITERIA

State	PH Limits	Test for Corrosion of Living Tissue	Test for Metal Corrosion
California - Hazardous Waste Criteria and Definitions	pH < 2 or ≥ 12	Yes 16 CFR 1500.41	--
Illinois - Tentative Land Disposal Criteria	where pH is < 3 or > 10 percent acidity or alkalinity must be determined	--	--
Kentucky - Draft Hazardous Waste Regulations	pH ≤ 3 or ≥ 12	--	Yes
Maine - Hazardous Waste Management Rules	pH ≤ 3 or ≥ 12	--	Yes
Michigan - Proposed Hazardous Waste Regulations	--	Yes 49 CFR 173.240	Yes
Minnesota - Hazardous Waste Regulations	pH < 3 or > 12	Yes 16 CFR 1500.41	Yes
Oregon - Draft Hazardous Waste Regulations	pH ≤ 3 or ≥ 12	49 CFR 173.240	Yes
Rhode Island - Proposed Hazardous Waste Generator Rules and Regulations	pH ≤ 3 or ≥ 12 (has provisions for liquids, solids and gases)	--	Yes

CORROSIVENESS - IDENTIFICATION CRITERIA

State	PH Limits	Corrosion of Living Tissue	Metal Corrosion
Tennessee - Proposed Hazardous Waste Regulations	pH $\leq$ 3 or $\geq$ 12	--	Yes
Texas - Hazardous Waste Guidelines: Waste Evaluation and Classification	pH < 2.5 or > 12	--	Yes
Washington - Hazardous Waste Regulations	pH < 3.0 or > 11.0 (substances which yield those pH levels when mixed with an equal weight of water)	--	Yes

APPENDIX B

EXAMPLES IN WHICH CORROSIVE WASTES CAUSED TISSUE DAMAGE

Pennsylvania 1975

An inspector attempting to halt unauthorized disposal of a drum in North Cordorus Township was splashed by the contents of the drum as it ruptured during compaction. The inspector sustained burns on the face and neck.

New Jersey 1974

During the first ten months of the year, seven chemical waste disposal injuries were noted in the logs of a landfill. Injuries included eye irritation and chemical burns from exposure to corrosive wastes.

Texas 1971

Barrels containing chemical wastes were caught in shrimpers' nets in the Gulf of Mexico. Physical damage to nets and equipment occurred, and exposed shrimper crewmen experienced skin burns and eye irritation.

APPENDIX C

CASE HISTORIES OF ACCIDENTS CAUSED BY MIXING OF INCOMPATIBLE WASTES (12)

1. Violent Reaction, Pressure Generation in Tank Truck

   In Richmond, California, a hazardous waste hauler mixed, in his 30-barrel tank truck, a liquid waste containing butyl acetate in xylene with an etching waste containing sulfuric acid, nitric acid and hydrofluoric acid. A hydrolysis reaction took place. The reaction generated pressure in the tank and blew the safety relief value while the truck was travelling through a residential area. A private residence was sprayed with the hazardous mixture. No one was injured, but considerable clean-up and repainting of the house was required.

2. Formation of Toxic Gas in Sanitary Landfill

   In Los Angeles County, a tank truck emptied several thousand gallons of cyanide waste onto refuse at a sanitary landfill. Another truck subsequently deposited several thousand gallons of acid waste at the same location. Reaction between the acid and the cyanide evolved large amounts of toxic hydrogen cyanide gas. A potential disaster was averted when a local chlorine dealer was quickly called to oxidize the cyanide with chlorine solution.

3. Formation of Toxic Gas in Excavated Site

   A load of acidic aluminum sulfate waste was inadvertently

discharged into an excavation already containing some sulfide waste. Hydrogen sulfide was released, and the lorry driver died in his cab at the landfill site.

4. Formation of Toxic Gas and Explosion in Waste Tank

Sulfide waste was added to a soluble oil waste in a tanker and subsequently added to other oily wastes in a tank. Later treatment of the oil with acid to break the emulsified oil resulted in evolution of hydrogen sulfide. Two operators were briefly affected by the gas. There was also an explosion in the tank.

5. Formation of Toxic Gas at a Landfill

At a sanitary landfill near Dundalk, Maryland, a 2,000 gallon liquid industrial waste load containing iron sulfide, sodium sulfide, sodium carbonate and sodium thiosulfate along with smaller quantities of organic compounds was discharged into a depression atop an earth-covered area of the fill. When it reached eight to ten feet below the point of discharge, the liquid started to bubble and fume blue smoke. The smoke cloud quickly engulfed the truck driver and disabled him. Several nearby workers rushed to his aid and were also felled. During the clean-up operation, one of the county fire-fighters also collapsed. All six of the injured were hospitalized and treated for hydrogen sulfide poisoning. It was not determined whether the generation of hydrogen

sulfide was due to the instability of the waste or the incompatibility of the waste with some of the landfill materials. The pH of the waste was measured to be 13 before it left the plant.

6. Formation of Toxic Gas in a Disposal Well

At a land disposal site in Southern California, a tanker was observed unloading a waste listed as "waste acid (5% HCl)" into a bottomless tank through an open stack above the ground. Shortly after the unloading operation commenced, yellowish-brown clouds of nitrogen dioxide began to emanate from the open stack. The reactions appeared to have subsided when the discharging of the wastes ceased. However, an hour later more NO_2 started to spew from the stack. The emission was halted by filling the stack with soil. There were no injuries, but the incident created a significant air pollution problem. Complaints from nearby business were received and a factory was evacuated.

7. Fire, Dispersal of Toxic Dusts from Leaky Containers

At a dump in Contra Costa County, California, a large number of drums containing solvents were deposited in a landfill. In the immediate area were leaky containers of concentrated mineral acids and several bags containing beryllium wastes in dust form. The operators failed to cover the waste at the end of the day. The acids reacted with the solvents during the night, ignited

them and started a large chemical fire. There was possible dispersion of beryllium dust into the environment. Inhalation, ingestion or contact with beryllium dust by personnel could have led to serious health consequences.

8. Violent Eruption in Waste Drum

At an engineering works, hot chromic acid waste was inadvertently added to a drum containing methylene chloride waste from degreasing operations. There was a violent eruption resulting in chemicals being sprayed locally in the workshop but no one was harmed.

9. Nitrogen Oxide Generation at a Sanitary Landfill

A truck driver picked up a load of "nitric acid" from an automotive specialities manufacturing company in early July 1976 and delivered it to a site in Southern California for well disposal. The well accepted approximately 50 gallons and then "pressurized". The driver then took the remainder of the load to another landfill in Southern California for trench disposal. Upon unloading, a reaction took place which generated brown nitrogen dioxide fumes which were carried by the wind and interfered with traffic 500 yards away. Towards the end of the month the same driver picked up another load of the same type from the same company and delivered it directly to the second landfill site. Upon arrival at the weigh station, he was instructed to tell the catapillar driver to "dig a deep hole". The catapillar operator dug a hole approxi-

mately 12 ft. deep, 12 ft. wide, and 20 ft. long into a previously filled area. The truck driver said that he observed damp ground and decomposing refuse in the trench. The driver then unloaded his truck and backed away from the trench as he did not want to be exposed to the hazard he had observed on the previous occasion. He observed a dense brown cloud emanating from the trench and could not return to his truck until its contents had been drained and the hazard reduced. A chemical analysis of the retained sample showed that it contained approximately 70% nitric acid and 5% hydrofluoric acid along with aluminum and chromium. The sample was fuming when it was taken from the truck.

10. Cyanide Generation at A Sanitary Landfill

A standard procedure at a Southern California disposal site for handling liquid wastes containing cyanides and spent caustic solutions was to inject these loads into covered wells dug into a completed section of a sanitary landfill. Routine air sampling in the vicinity of the wells detected low levels of HCN. Sampling in the well head detected more than 1000 ppm HCN. No cyanide was detected during addition of the spent caustic to a new well. On the basis of these discoveries, use of the wells was discontinued. The cyanide gas was apparently formed in the well as a result of lowering of the pH of the waste by CO_2 and organic acids produced

in the decomposition of refuse.

11. Nitric Acid and Alcohol Cause Explosion of Tank Car

While transfering 64% nitric acid to a supposedly empty tank car, the tank car exploded. An investigation revealed that the tank car contained a small residual of alcohol which was converted to acetaldehyde by the acid. The heat of reaction vaporized the acetaldehyde and subsequently ignited the acetaldehyde-air mixture causing an explosion. No injuries or fatalities resulted.

12. Nitric Acid - Ammonia Fire Generate Toxic Fumes

In a Carroll County, Arkansas fertilizer warehouse, a mixture of ammonia and nitric acid ignited and destroyed the plant. Toxic fumes generated by the blaze forced the evacuation of the town's residents. No injuries or fatalities were reported.

13. Vacuum Truck Rupture Caused by Formation of Hydrogen Gas

In Los Angeles, a vacuum truck containing an unknown quantity of residual wastes picked-up a spent sulfuric acid metal stripping solution. On the way to the disposal site a violent explosion ocurred, rupturing the tank and injuring the driver. Subsequent investigation revealed that the residue in the tank prior to the pick-up of the acid solution contained aluminum and magnesium turnings and fines. The action of the acid on these metal particles produced hydrogen gas and heat. Extreme pressure build-up resulted in the violent rupture of the tank.

APPENDIX D

REACTIONS BETWEEN ACIDS OR BASES AND OTHER SUBSTANCES-POSSIBLE ADVERSE CONSEQUENCES (12)

MINERAL ACIDS + ALCOHOLS AND GLYCOLS

Dehydration reactions and displacement with the halide result in heat generation.

MINERAL ACIDS + ALDEHYDES

Condensation reactions cause heat generation. Acrolein and other unsaturated aldehydes polymerize readily.

MINERAL ACIDS + AMIDE

Hydrolysis of amide to the corresponding carboxylic acid results in an exotherm.

MINERAL ACIDS + AMINES

The acid base reaction between these two types of compounds forming the ammonium salts may be sufficiently exothermic to cause a hazard.

MINERAL ACIDS + AZO COMPOUNDS

Amyl azo and diazo compounds decompose exothermically upon mixing with strong mineral acids to yield nitrogen gas and the corresponding amyl cation. Aliphatic azo and diazo compounds, particularly diazoalkanes, can polymerize violently with heat generation. Organo azides can also decompose exothermically with strong acid to form nitrogen gas and the respective cations. An exotherm also results from the acid-base reaction of hydrazines with mineral acids

as hydrazines are comparable in base strength to ammonia. Diazomethane is a particularly reactive compound in this group.

MINERAL ACIDS + CARBAMATES

Carbamates can undergo hydrolysis as well as decarboxylation upon mixing with strong mineral acids. Both reactions are exothermic and the latter can generate pressure if it occurs in a closed container.

MINERAL ACIDS + CAUSTICS

The acid-base reaction between strong mineral acids and strong caustics is extremely exothermic and can be violent. Fires can result if the caustic substance is an alkoxide.

MINERAL ACIDS + CYANIDE

Inorganic cyanides rapidly form extremely toxic and flammable hydrogen cyanide gas upon contact with mineral acids.

MINERAL ACIDS + DITHIOCARBAMATES

Acid hydrolysis of dithiocarbamate heavy metal salts with strong mineral acids yields extremely flammable and toxic carbon disulfide gas. An exotherm can be expected from the reaction.

MINERAL ACIDS + ESTERS

Strong mineral acids in excess will cause hydrolysis and decomposition of esters with heat generation.

MINERAL ACIDS + ETHERS

Ether may undergo hydrolysis with strong acids exothermically.

MINERAL ACIDS + FLUORIDES

Most inorganic fluorides yield toxic and corrosive hydrogen fluoride gas upon reaction with strong mineral acids.

MINERAL ACIDS + HALOGENATED ORGANICS

Strong mineral acids in excess may cause decomposition with generation of heat and toxic fumes of hydrogen halides.

MINERAL ACIDS + ISOCYANATES

Acid catalyzed decarboxylation as well as vigorous decomposition can occur upon mixing of isocyanates with strong mineral acids.

MINERAL ACID + KETONE

Acid catalyzed aldol condensation occurs exothermically.

MINERAL ACIDS + MERCAPTANS

Alkyl mercaptans are particularly reactive with mineral acids yielding extremely toxic and flammable hydrogen sulfide gas. Other mercaptans can yield hydrogen sulfide with excess strong acids. Excess strong acid can also result in decomposition and generation of toxic fumes of sulfur oxides.

MINERAL ACIDS + ALKALI AND ALKALINE EARTH METALS

The reaction of strong mineral acids with alkali and alkaline earth metals in any form will result in a vigorous exothermic generation of flammable hydrogen gas and possible fire.

MINERAL ACIDS + METAL POWDERS, VAPORS, OR SPONGES

Reactions of strong mineral acids with finely divided metals or metals in a form with high surface area will result

in vigorous generation of flammable hydrogen gas and possible explosion caused by the heat of reaction.

MINERAL ACIDS + METAL SHEETS, RODS, DROPS, ETC.

Strong mineral acids will form flammable hydrogen gas upon contact with metals in the form of plates, sheets, chunks, and other bulk forms. The heat of reaction may ignite the gas formed.

MINERAL ACIDS + NITRIDES

The aqueous fraction of strong mineral acids will react with nitrides evolving caustic and flammable ammonia gas. The acid-base reaction of mineral acids and nitrides can also evolve much heat and ammonia.

MINERAL ACIDS + NITRILES

Exothermic hydrolysis of nitriles to the corresponding carboxylic acid and ammonium ion is known to occur with mineral acids. Extremely toxic and flammable hydrogen cyanide gas may be evolved with such compounds as acetone, cyanohydrin and propionitriles.

MINERAL ACIDS + UNSATURATED ALIPHATICS

Addition of mineral acids to alkenes usually results in exothermic acid catalyzed hydration and partial addition of the hydrogen halide or sulfates. Acetylenes are also susceptible to exothermic acid catalyzed hydration, forming the corresponding aldehyde or ketone with possible addition of the hydrogen halide in the case of halogen acids.

MINERAL ACIDS + ORGANIC PEROXIDES

Strong mineral acids can react with organic peroxides and

hydroperoxides with enough heat generated to cause explosive decomposition in the more unstable compounds. Oxygen can also be generated.

MINERAL ACIDS + PHENOLS AND CRESOLS

Exothermic sulfonation reactions can occur with addition of sulfonic acid to phenols and cresols. Substitution of the hydroxyl with a halide can occur with addition of the halogen acids. Excess strong acid can decompose phenols and cresols with heat generation.

MINERAL ACID + ORGANOPHOSPHATES

Excess strong mineral acid can cause decomposition of organophosphates, phosphothioate and phosphodithioates with heat generation and possible toxic gas formation.

MINERAL ACIDS + SULFIDES

Extremely toxic and flammable hydrogen sulfide gas results from the combination of mineral acids and sulfides.

MINERAL ACIDS + EPOXIDES

Acid catalyzed cleavage can occur, initiating polymerization with much heat generated.

MINERAL ACIDS + COMBUSTIBLE MATERIALS

Dehydration and decomposition on addition of excess strong mineral acid can cause heat and possible toxic gas generation.

MINERAL ACIDS + EXPLOSIVES

Many explosives are extremely heat sensitive and can be detonated by heat generated from the action of strong mineral acids on these compounds.

MINERAL ACIDS + POLYMERIZABLE COMPOUNDS

Strong mineral acids can act as initiators in the polymerization of these compounds. The reactions are exothermic and can occur violently.

MINERAL ACIDS + STRONG OXIDIZING AGENTS

Many combinations of strong mineral acids and strong oxidizing agents are sensitive to heat and shock and may decompose violently. The halogen acids may be oxidized yielding highly toxic and corrosive halogen gases, accompanied by heat generation.

MINERAL ACIDS + STRONG REDUCING AGENTS

Many reducing agents form flammable hydrogen gas on contact with mineral acids. The heat generated can cause spontaneous ignition. Some reducing agents such as metal phosphides and inorganic sulfides evolve extremely toxic and flammable fumes of phosphine and hydrogen sulfides, respectively.

MINERAL ACIDS + WASTE AND MISCELLANEOUS AQUEOUS MIXTURES

Much heat can be evolved upon solubilization and hydrolysis of these acids.

OXIDIZING MINERAL ACIDS + ORGANIC ACIDS

These mineral acids can oxidize the hydrocarbon moeity of organic acids with resulting heat and gas formation.

OXIDIZING MINERAL ACIDS + ALCOHOLS AND GLYCOLS

Oxidation of the hydrocarbon moeity can occur resulting in heat and gas formation. Nitration with nitric acid can take place in the presence of sulfuric acid forming extremely unstable nitro compounds.

OXIDIZING MINERAL ACIDS + ALDEHYDES

Oxidation of the hydrocarbon moeity can occur resulting in heat and gas formation.

OXIDIZING MINERAL ACIDS + AMIDES

Oxidation with excess acid can result in heat generation and formation of toxic fumes of nitrogen oxides.

OXIDIZING MINERAL ACIDS + AMINES

The acid-base reaction produces much heat and exhaustive oxidation results in generation of heat and toxic fumes of nitrogen oxide.

OXIDIZING MINERAL ACIDS + AZO COMPOUNDS

Azo compounds and diazo compounds are easily decomposed by strong acids evolving much heat and nitrogen gas. They are very susceptible to oxidation and can evolve toxic fumes of nitrogen oxides upon exhaustive oxidation. Hydrazines are expecially susceptible to oxidation and inflame upon contact with oxidizing agents. Many of the compounds in this group such as diazomethane and the azides are very unstable and can decompose explosively upon heating.

OXIDIZING MINERAL ACIDS + CARBAMATES

Carbamates can undergo exothermic hydrolysis and decarboxylation upon mixing with these acids. Exhaustive oxidation can also result in formation of toxic fumes of nitrogen oxides, and sulfur oxides in the case of thiocarbamates.

OXIDIZING MINERAL ACIDS + CAUSTICS

The neutralization reaction can be violent with evolution of much heat.

OXIDIZING MINERAL ACIDS + CYANIDES

Evolution of extremely toxic and flammable hydrogen cyanide gas will occur before oxidation.

OXIDIZING MINERAL ACIDS + DITHIOCARBAMATES

Acids will cause decomposition of dithiocarbamates with evolution of extremely flammable carbon disulfide. Significant heat may be generated by the oxidation and decomposition to ignite the carbon disulfide.

OXIDIZING MINERAL ACIDS + ESTERS

Exhaustive oxidation of esters can cause decomposition with heat and possible ignition of the more flammable esters. Conversion to the organic acid and decarboxylation can also occur.

OXIDIZING MINERAL ACIDS + ETHERS

Heat generated from the exhaustive oxidation of ethers can ignite the more flammable ethers. These compounds can also undergo exothermic acid catalyzed cleavage.

OXIDIZING MINERAL ACIDS + FLUORIDES

Gaseous hydrogen fluoride can result from a combination of inorganic fluorides and these acids. Hydrogen fluoride is extremely corrosive and toxic. Some heat can also be evolved.

OXIDIZING MINERAL + HALOGENATED ORGANICS

These acids can cause oxidation and decomposition of halogenated organics resulting in heat and generation of extremely toxic fumes of hydrogen chloride, phosgene, and other gaseous halogenated compounds.

OXIDIZING MINERAL ACIDS + ISOCYANATES

Isocyanates may be hydrolyzed by the water in concentrated acids to yield heat and carbon dioxide. They may also be oxidized by these acids to yield heat and toxic nitrogen oxides.

OXIDIZING MINERAL ACIDS + KETONES

Ketones can undergo exothermic aldol condensations under acidic conditions. Oxidizing acids can cleave the ketone to give a mixture of acids. Excess acid can cause complete decomposition yielding much heat and gas. Fire can also result.

OXIDIZING MINERAL ACIDS + MERCAPTANS

Extremely toxic and flammable hydrogen sulfide gas can be formed by the action of the acid on mercaptans. Oxidation of mercaptans and other sulfur compounds can result in formation of toxic sulfur dioxide and heat.

OXIDIZING MINERAL ACIDS + ALKALI AND ALKALINE EARTH METALS

Extremely flammable hydrogen gas can be generated upon contact of acids and these metals. The reaction of such a strong oxidizing agent and strong reducing agents can be so violent as to cause a fire and possibly an explosion.

OXIDIZING MINERAL ACIDS + METAL POWDERS, VAPORS, AND SPONGES

The action of acid on these metals produces hydrogen gas and heat. Due to the large surface area of these forms of metals, the reaction can occur with explosive violence.

OXIDIZING MINERAL ACIDS + METAL SHEETS, RODS, DROPS, ETC.

The reaction of acids on metals as sheets, plates, and other

bulk forms can evolve hydrogen gas and some heat. Although the reaction proceeds much slower than in the case of powders, a definite fire hazard exists. Many metals are attacked by nitric acid.

OXIDIZING MINERAL ACIDS + NITRIDES

Nitrides are extremely strong bases and will participate in an acid-base reaction evolving much heat. This reaction can proceed with explosive violence due to the instability of metal nitrides and the generation of flammable ammonia gas.

OXIDIZING MINERAL ACIDS + NITRILES

The primary hazard in mixing these types of compounds appears to be oxidation of the nitriles with generation of heat and toxic fumes of nitrogen oxides. In some cases such as acetone cyanohydrin and propionitrile, extremely toxic hydrogen cyanide gas is known to result from mixing with strong acids. These fumes are also flammable. Mixtures of nitric acid and acetonitrile are high explosives.

OXIDIZING MINERAL ACIDS + NITRO COMPOUNDS

These acids can decompose nitro compounds to produce heat and toxic fumes of nitrogen oxide. This oxidation can be extremely violent. Mixtures of nitric acid and nitro-aromatics are known to exhibit explosive properties. Mixtures of some nitroalkanes (nitromethane) with nitric acid can also be detonated.

OXIDIZING MINERAL ACIDS + UNSATURATED ALIPHATICS

Aliphatic unsaturated hydrocarbons are extremely susceptible to oxidation resulting in heat generation and fire.

OXIDIZING MINERAL ACIDS + SATURATED ALIPHATICS

Aliphatic saturated hydrocarbons are easily oxidized by these acids yielding heat and carbon dioxide.

OXIDIZING MINERAL ACIDS + ORGANIC PEROXIDES

The lower molecular weight organic peroxides and hydroperoxides are very sensitive to heat and shock. Mixing of oxidizing mineral acids with such unstable compounds can cause heat generation due to the oxidizing capacity of the acids and acid catalyzed hydrolysis. These reactions can cause explosive decomposition.

OXIDIZING MINERAL ACIDS + PHENOLS AND CRESOLS

Phenols and cresols are easily oxidized and excess oxidizing acids can result in much heat generation.

OXIDIZING MINERAL ACIDS + ORGANOPHOSPHATES

Excess oxidizing acid can decompose these compounds to yield heat and toxic fumes of nitrogen oxides, sulfur oxides, and phosphorous oxides.

OXIDIZING MINERAL ACIDS + WATER AND WATER MIXTURES

Much heat can be evolved from the dissolution of these acids by water.

OXIDIZING MINERAL ACIDS + SULFIDES

Toxic and flammable hydrogen sulfide gas can be generated by the action of these acids on inorganic sulfides. These sulfides can also be oxidized exothermically to sulfur dioxide, also a toxic gas. This reaction can occur very violently.

OXIDIZING MINERAL ACIDS + EPOXIDES

Epoxides are very easily cleaved by acids with heat generation.

This ring opening can be the initiating step in the formation of epoxy resins, and uncontrolled polymerization can result in extreme heat generation. The oxidation capacity of these acids can cause ignition of the epoxides.

OXIDIZING MINERAL ACIDS + COMBUSTIBLE MATERIALS

Oxidizing mineral acids can decompose some substances with heat generation and possible fire. Toxic gases may also be formed as combustion products, but the type of gas will depend upon the composition of these miscellaneous substances.

OXIDIZING MINERAL ACIDS + EXPLOSIVES

Such strong acids can easily detonate compounds in this group of explosives due to the heat generated upon mixing. The oxidizing character of these acids merely enhances the possibility of detonation.

OXIDIZING MINERAL ACIDS + POLYMERIZABLE COMPOUNDS

These acids can act as initiators in the polymerization of many compounds. These reactions are exothermic and can occur violently. In addition, these acids can oxidize certain compounds producing more heat and possible toxic fumes.

OXIDIZING MINERAL ACIDS + STRONG REDUCING AGENTS

Mixing of compounds in these two groups can result in very violent, extremely exothermic reactions. Fires and explosions can result.

ORGANIC ACIDS + ALDEHYDES

Exothermic condensation reactions can occur between these two types of compounds. The acidic character of the organic

acids may be sufficient to catalyze the reaction. Polybasic and unsaturated acids are susceptible to polymerization under these condition, resulting in much heat generated.

ORGANIC ACIDS + AMINES

An acid-base reaction between the stronger acids and amines can generate some heat. Dicarboxylic acids and diamines can copolymerize with heat generation.

ORGANIC ACIDS + AZO COMPOUNDS

Aliphatic and aromatic diazo compounds are readily decomposed by organic acids releasing heat and nitrogen gas as reaction products. Azo compounds are not sensitive to such decomposition. Hydrazine azide is extremely sensitive to heat or shock. An acid-base reaction with hydrazine can produce some heat.

ORGANIC ACIDS + CAUSTICS

Acid-base reactions produce heat.

ORGANIC ACIDS + CYANIDES

Hydrogen cyanide, an extremely toxic and flammable gas, is generated upon mixing.

ORGANIC ACIDS + DITHIOCARBAMATES

Toxic and flammable carbon disulfide can be formed upon contact of dithiocarbamate with the stronger organic acids. Although CS_2 is a liquid at room temperature, it has a very high vapor pressure. Some heat can be generated from the hydrolysis of the dithiocarbamate salts.

ORGANIC ACIDS + FLUORIDES

Toxic and corrosive hydrogen fluoride fumes can be generated by the action of strong organic acids upon metal fluoride

salts. Alkali metal fluorides are expecially susceptible to decomposition in this manner.

ORGANIC ACIDS + ISOCYANATES

Some water is normally associated with organic acids, and this can cause hydrolysis of isocyanates to carbon dioxide and amines with some heat generated.

ORGANIC ACIDS + ALKALI AND ALKALINE EARTH METALS

Reaction of organic acids with these metals in any form can result in exothermic generation of flammable hydrogen gas and possible fire.

ORGANIC ACIDS + METAL POWDERS, VAPORS, AND SPONGES

The stronger organic acids can liberate flammable hydrogen gas upon contact with metals in these forms. The heat of reaction can cause explosions.

ORGANIC ACIDS + NITRIDES

An acid-base reaction can occur resulting in heat and possible evolution of flammable ammonia gas. Many of these nitrides are explosively unstable and can be detonated by the heat of reaction.

ORGANIC ACIDS + NITRILES

Strong organic acids can convert nitriles to their corresponding organic acid with some heat generation.

ORGANIC ACIDS + SULFIDES

Extremely toxic and flammable hydrogen sulfide and some heat can be generated.

ORGANIC ACIDS + EPOXIDES

Acid catalyzed cleavage of the epoxide ring can initiate

violent polymerization with much heat generated.

ORGANIC ACIDS + EXPLOSIVES

Strong organic acids can decompose compounds in this group resulting in enough heat to cause detonation.

ORGANIC ACIDS + POLYMERIZABLE COMPOUNDS

Strong organic acids can initiate cationic polymerization. Dicarboxylic acids can copolymerize with diamines as in the reaction of adipic acid and hexamethylene diamine to form Nylon 6,6.

ORGANIC ACIDS + OXIDIZING AGENTS

The hydrocarbon moeity of the organic acids are susceptible to decomposition by strong oxidizing agents releasing heat and gas. The gas produced can be toxic if the acid contains halogens such as dichlorophenoxy acetic acid, or if it contains other hetero atoms.

ORGANIC ACIDS + REDUCING AGENTS

Carboxylic acids are easily reduced by lithium aluminum hydride to the corresponding alcohols with some heat generation. Other reducing agents require more vigorous reaction conditions. Flammable hydrogen gas can be produced from the extractions of the hydroxyl proton and the β-hydrogens.

CAUSTICS + ESTERS

Esters are easily hydrolyzed by caustics to a salt and alcohol with heat generation.

CAUSTICS + HALOGENATED ORGANICS

Aliphatic halides can undergo substitution or dehydrohalogenation upon treatment with strong caustics. Both

processes involve some heat generation while the second evolves flammable olefins and acetylenes, especially with the lower molecular weight compounds. Halogenated aromatics, however, are relatively stable to strong caustics.

CAUSTICS + ISOCYANATES

Caustics catalyze the polymerization of diisocyanates yielding much heat. The mono isocyanates decompose to amines and carbon dioxide upon contact with caustics.

CAUSTICS + KETONES

Caustics can catalyze the self-condensation of ketones, yielding heat.

CAUSTICS + ALKALI AND ALKALINE EARTH METALS

Heat and flammable hydrogen gas can be generated due to the aqueous nature of most caustics.

CAUSTICS + METAL POWDERS, VAPORS, AND SPONGES

Heat and flammable hydrogen gas may be generated with some metals such as aluminum, magnesium, zinc, and beryllium. Explosions may also occur due to the high surface area of these forms.

CAUSTICS + NITRO COMPOUNDS

Nitro alkanes and caustics form salts in the presence of water. The dry salts are explosive.

CAUSTICS + ORGANOPHOSPHATES

Alkaline hydrolysis of phosphorothioates can generate enough heat to cause explosive rearrangement from the thiono to the thiolo form. Hydrolysis of other organophosphates can generate heat.

CAUSTICS + EPOXIDES

Base catalyzed cleavage can result in polymerization with much heat.

CAUSTICS + EXPLOSIVES

Alkaline hydrolysis or other reactions can generate enough heat to detonate these compounds.

CAUSTICS + POLYMERIZABLE COMPOUNDS

These compounds can undergo anionic polymerization with caustics as initiators yielding much heat.